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MOLYBDENUM DISULFIDE AS A LUBRICANT AND CATALYST IN ADAPTIVE NANOCOMPOSITE COATINGS (PREPRINT)

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14. ABSTRACT
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Molybdenum disulfide as a lubricant and catalyst in adaptive nanocomposite coatings

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Abstract

Nanocomposite YSZ-Ag-Mo-MoS_2 with different MoS_2 additions (0-100 atomic percent) coatings were deposited with a hybrid pulsed laser/magnetron sputtering/filtered cathodic arc process. Wear testing was performed from 25-700 °C for each of the coatings. Electron microscopy and other characterization techniques were used to examine the surfaces and wear tracks of the coatings to determine the mechanisms resulting in the measured tribological properties. Adaptive coatings containing 8 atomic percent MoS_2 demonstrated a friction coefficient of 0.2 throughout the temperature range examined here, compared to 0.4 for YSZ-Ag-Mo with no MoS_2. Characterization of the YSZ-Ag-Mo-8%MoS_2 coating revealed that MoS_2 and silver provided lubrication at temperatures ≤ 300 °C, while silver molybdate phases and MoO_3 were lubricious at higher temperatures. Silver molybdate was not observed in the coatings containing 0% MoS_2. The role of sulfur in the formation of silver molybdate is briefly discussed.

Introduction

Adaptive nanocomposites, also known as “chameleon coatings,” are a class of materials that automatically adjust surface composition and structure to minimize friction as the ambient environment changes [1-3]. Adaptation results from the transformation of amorphous and nanocrystalline inclusions into lubricious macro-phases in the friction contact when exposed to changes in temperature, relative humidity, and/or wear. A series of adaptive coatings incorporating metals in a nanocrystalline/amorphous yttria-stabilized zirconia (YSZ) matrix were designed for use as solid lubricants from 25-700 °C. These coatings incorporated soft noble metals for lubrication at low to moderate temperatures (<500 °C) [4-12], and transition metals expected to form lubricous oxides at higher temperatures in air [13-15]. For example, a YSZ-Ag-Mo nanocomposite adaptive coating provides lubrication by forming a silver rich surface at 300-500 °C, and MoO_3 at temperatures above 500 °C, resulting in a friction coefficient of ≤ 0.4 from 25 to 700 °C [9]. Silver molybdate compounds, yielding a friction coefficient of ≈ 0.2, were expected to form when the YSZ-Ag-Mo coatings were heated to 500 °C or higher [16,17], however, no such compounds were detected. In the current work, YSZ-Ag-Mo nanocomposite coatings with MoS_2 nanoinclusions were grown to reduce friction at low temperature and to promote silver-molybdenum reactions. Coatings with different MoS_2 contents were subjected to wear testing at 25-700 °C. The surfaces and wear tracks of the coatings were analyzed and compared to YSZ-Ag-Mo (0% MoS_2) and pure MoS_2 coatings after testing at elevated temperatures to identify the operative lubrication mechanisms.

Experimental procedure

Coatings composed of yttria stabilized zirconia (YSZ), silver, molybdenum and different concentrations of molybdenum disulfide were deposited with a hybrid filtered vacuum arc/pulsed laser/magnetron sputtering technique [18-20], with parameters similar to those described previously [18]. The filtered vacuum arc source was fitted with a titanium cathode and used to clean the substrates with metal ions and to deposit a 50 nm Ti adhesion layer. YSZ and MoS_2 were deposited by pulsed laser ablation of a segmented 5 cm diameter disk for all composite coatings. The number and size of the segments comprising the disk were varied to alter the composition of the coatings. Programmable mirrors were used to direct the laser to random positions on the surface of the rotating target. Silver and molybdenum were incorporated into the materials via magnetron sputtering from pure metal targets. The pure MoS_2 coating was also deposited by magnetron sputtering of a solid MoS_2 target in pure argon. The compositions of the as-deposited coatings were measured with X-ray photoelectron spectroscopy (XPS) after sputter cleaning each sample with 5000 eV Ar^+ ions for 15 seconds. All coatings contained approximately 20 atomic percent silver and 10 atomic percent molybdenum, with the exception of the pure MoS_2 coating.

Friction coefficients in laboratory air (20-30% relative humidity) were measured with a high temperature ball-on-disc tribometer using a 6.35 mm diameter silicon nitride ball with a 1 N load. The sliding rate was 0.2 m s^{-1}, with the disk rotating clockwise at 200 rpm for all tests. The thermocouple inside the tribometer oven was calibrated before testing for each temperature of interest with a separate thermocouple spot-welded to an uncoated substrate, which was placed into the sample test location and heated without rotation. Wear tests were started after coating samples were heated to the desired temperature (20-25 minutes heating time) and allowed to equilibrate at the target temperature for 5-10 minutes. A sample of each coating was tested for 10000 cycles or to failure (whichever came first) at 25, 300, 500 and 700 °C. Coating failure was defined by a sharp increase in the friction coefficient equal to or greater than that of the uncoated substrate alone. Selected samples were also worn for only 1000 cycles to allow examination of the wear track before coating failure. Upon completion of the ball-on-disk tests, samples were immediately removed from the furnace and allowed to cool naturally in air. A new coating sample was used for each wear test to observe the adaptive behavior from the as-deposited condition. Coatings deposited on 440C steel substrates were used for wear tests at 25 and 300 °C, M50 substrates were selected for testing at 500 °C, and Inconel 718 substrates were used for all 700 °C tests. The coefficients of friction for each polished, uncoated substrate were also measured to allow identification of coating failure.

Wear tracks and surfaces on the worn samples were examined with scanning electron microscopy (SEM), energy dispersive spectroscopy (EDS), glancing angle X-ray diffraction, XPS and micro-Raman spectroscopy to characterize changes in surface structure and composition after testing at different temperatures. Peaks in the Raman spectra were identified using data found in Reference 21, in addition to that presented by Gulbinski et al. [17].

Results

Table I lists the composition, friction coefficient and cycles to failure at temperatures between 25-700 °C for YSZ-20%Ag-10%Mo coatings with different MoS_2 additions. The YSZ-Ag-Mo coating (0% MoS_2) maintained a friction coefficient of ≈ 0.4 for all temperatures. Adding MoS_2 reduced the coefficient of friction of the coating throughout the examined temperature range. The YSZ-Ag-Mo coating with 8 atomic percent MoS_2 was the only coating that demonstrated a friction coefficient of less than 0.2 for all temperatures. Pure MoS_2 yielded a significantly lower friction coefficient of <0.1 at 25 and 300 °C, but failed immediately at temperatures above 300 °C.

Figures 1 a-e show the morphological response of coatings with different MoS_2 content at moderate and high temperatures. The YSZ-Ag-Mo coating formed a continuous silver layer at 300 °C, resulting from diffusion of silver from the coating to the surface as described previously [9] and shown in Figure 1a. Smearing of the silver layer, with a low shear strength at 300 °C [5-7,11,22], was observed in the wear track (Fig. 1a). Figure 1b shows that silver was pushed out of the wear track under the ball contact pressure at 700 °C, exposing the molybdenum in the underlying coating to air, and resulting in the formation of lubricious molybdenum trioxide crystals, which were apparent as faceted crystals adjacent to the smeared MoO_3 in the friction contact [18]. For the YSZ-Ag-Mo with 8 atomic percent MoS_2, equiaxed grains appeared to have grown on the coating surface, similar to that observed for the coatings with no MoS_2, however, a stick-like phase was also spread homogenously among these grains away from the wear tracks (Figs. 1 c-d). In the wear track of the sample tested at 300 °C, plastic deformation of a soft phase and the presence of a darker, smeared phase at the surface of the wear track were apparent (Fig. 1c). At 700 °C, the presence of a slightly different stick-like phase on the surface away from the wear track was observed (Fig. 1d). In the wear track of the sample tested at 700 °C, deformed equiaxed grains over faceted crystals were visible. The pure MoS_2 coating surface showed few features at the surface after heating to 300 °C (Fig. 1 e), with smearing of the lubricous MoS_2 in the wear track. At 700 °C, more pronounced crystal growth was observed on the coating surface (Fig. 1f). In the wear track, the substrate is visible under the failed coating.

Figures 2(a-f) show glancing angle X-ray diffractograms for the (a,b) 0, (c,d) 8, and (e,f) 100 atomic percent MoS_2 coatings after wear testing at 300 and 700 °C for ≈ 60 minutes. Silver was the only phase detected for the 0% MoS_2 coatings heated to any temperature ≥ 300 °C (Fig. 2a-b). For the adaptive coatings containing MoS_2 however, Ag_2MoO_4 (PDF #08-0473) and $Ag_2Mo_2O_7$ (PDF # 21-1339) silver molybdate phases and MoO_3 phases (PDF #47-1320) were present after heating to temperatures >300 °C, as shown in Figure 2d. X-ray diffraction of the 100 percent MoS_2 coating heated to 300 °C showed broad MoS_2 peaks (Fig. 2e).). For the sample heated to 700 °C, the same MoS_2 peaks (PDF #37-1492) were sharper and MoO_3 peaks were also detected on the sample surface (Fig. 2f).

To identify the phases present in selected wear tracks, micro-Raman spectroscopy was employed. Figure 3a shows that the crystals similar to those in the wear track of YSZ-20%Ag-10%Mo coating tested at 700 °C (Fig. 1b) were indeed MoO_3 [21]. The Raman spectrum in 3b shows that the dark spots observed in the YSZ-20%Ag-10%Mo-8%MoS_2 coating heated to 300

°C (Fig. 1c) were composed of MoS_2 [21]. Figure 3c shows that the phase in the wear track for the 8% MoS_2 coating heated to 700 °C consists of the same silver molybdate and molybdenum trioxide phases detected by x-ray diffraction on the coating surface.

Discussion

Comparison of the adaptive nanocomposites with and without MoS_2 shows that the addition of MoS_2 to the YSZ-Ag-Mo adaptive coatings reduced friction. Figure 1c coupled with the Raman spectrum in Figure 3b reveals that reduced friction at moderate temperatures (<300 °C) results from MoS_2 lubrication of an already lubricious silver surface. At higher temperatures however, it appears that MoS_2 facilitated the reaction of the Ag and Mo in the coating with ambient oxygen to produce the silver molybdate compounds Ag_2MoO_4 and $Ag_2Mo_2O_7$. These compounds only appeared in coatings containing MoS_2, and were not found in the single YSZ-20Ag-10Mo composites studied here, nor in any other composition of YSZ-Ag-Mo reported on previously [9,18]. Gulbinski et al. [17] reported on the low friction coefficients of these compounds between 300-600 °C consistent with those measured in the present work, with friction increasing at higher temperatures. The YSZ-Ag-Mo-MoS_2 coatings in the current work probably maintained a low friction (<0.2) coefficient at higher temperatures due to the formation of MoO_3 coupled with the other lubricious silver molybdate phases identified by X-ray diffraction and Raman spectroscopy. The same MoO_3 phase resulting from oxidation of the pure MoS_2 coating did not, however, yield the same low friction coefficient at 700 °C. Failure of MoS_2 at temperatures above 300 °C, is consistent reports that 300-400 °C is the limit of MoS_2 as an effective lubricant [22]. The wear lifetimes of coatings with MoS_2 additions were also relatively short, however previous work [23,24] has shown that alternating the 0% MoS_2 adaptive coating with TiN diffusion barrier layers in a multilayer stack resulted in an order-of-magnitude lifetime improvement. It is expected that the coatings with MoS_2 additions will demonstrate similar behavior.

While the exact mechanism leading to formation of silver molybdate compounds in the presence of sulfur is not yet entirely clear, Li et al. [25] have shown that heating of a Ag/S/Mo system results in the reaction $MoS_x + Ag \rightarrow AgMoS_x$ upon heating to temperatures above room temperature. In air, at temperatures above 500 °C, it is possible that the sulfur was then replaced with oxygen to form the molybdate. Details of the mechanisms resulting in the ultimate composition of the coatings are currently being studied, however, it is suspected that the stick-like phase observed on the surface of YSZ-Ag-Mo-MoS_2 coatings after heating was a by-product of silver molybdate formation. Compositional analysis of these small features may be useful for determining the silver molybdate reaction pathway.

Conclusions

Friction coefficients of YSZ-Ag-Mo adaptive nanocomposite coatings with different MoS_2 additions were measured from 25-700 °C, and correlated to the composition and microstructural evolution of the coatings during testing. Adding 8% MoS_2 to the YSZ-Ag-Mo coatings resulted in a decrease in the friction coefficient from 0.4 to 0.2 from 25-700 °C. Lower friction from 25-300 °C resulted from MoS_2 lubrication. At higher temperatures the MoS_2 additions did not directly provide lubrication, but rather promoted the formation of lubricious silver molybdate phases at the coating surface.

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List of Figure Captions

Figure 1: Scanning electron micrographs of the wear tracks and surfaces of the (a-b) 0% MoS_2, (c-d) 8% MoS_2, and 100 % MoS_2 coatings after wear testing at 300 and 700 °C, respectively. The insets with black borders show the surfaces away from the wear tracks, and the insets surrounded by white show a higher magnification view of the highlighted wear track feature.

Figure 2: Glancing incidence X-ray diffractograms of the (a-b) 0% MoS_2, (c-d) 8% MoS_2, and (e-f) 100% MoS_2 coatings after wear testing at 300 and 700 °C, respectively.

Figure 3: Raman spectra for the (a) 0% MoS_2 coating tested at 700 °C and (b-c) the 8% MoS_2 coating tested at 300 and 700 °C, respectively. The inset micrograph shows a feature similar to those the laser was focused upon to produce the corresponding spectra.

Table I: Average friction coefficients and cycles-to-failure for YSZ-Ag-Mo coatings with different MoS_2 additions.

	friction coefficient				cycles to failure			
	25 °C	300 °C	500 °C	700 °C	25°C	300°C	500 °C	700 °C
Atomic percent MoS_2								
0	0.4	0.3	0.4	0.4	>10000	>10000	4000	>10000
4	0.5	0.2	0.2	0.3	>10000	>10000	1000	1000
8	0.2	0.1	0.2	0.2	>10000	>10000	3000	5000
100	0.04	0.06	-	-	>10000	>10000	<100	<100

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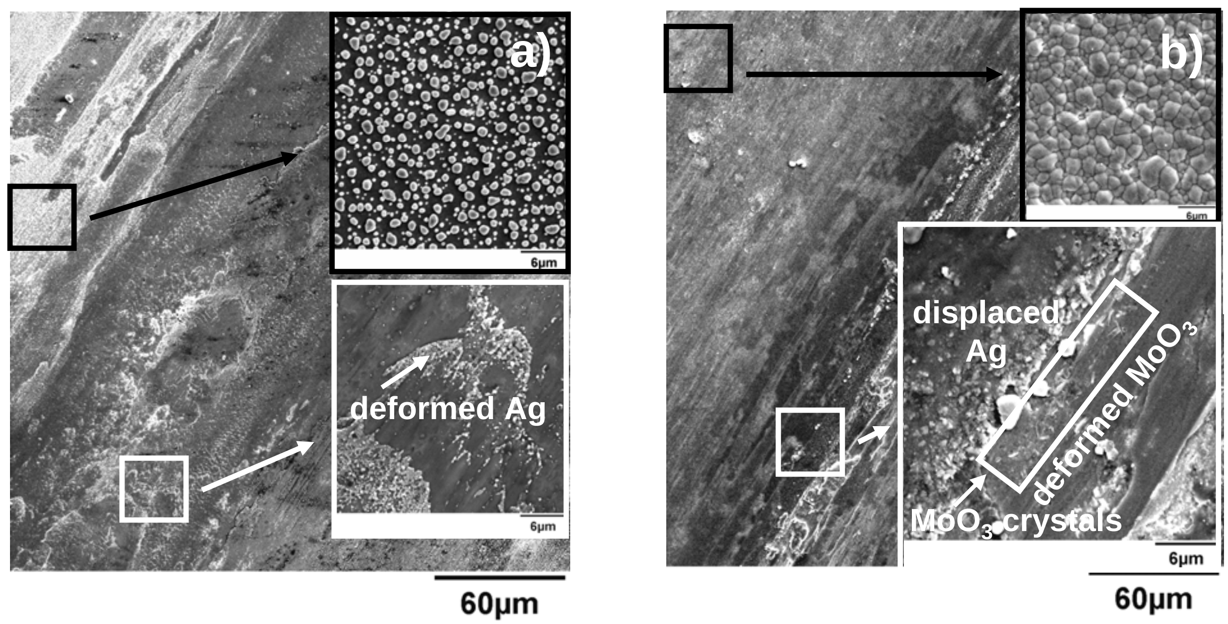
Figures 1 a-b



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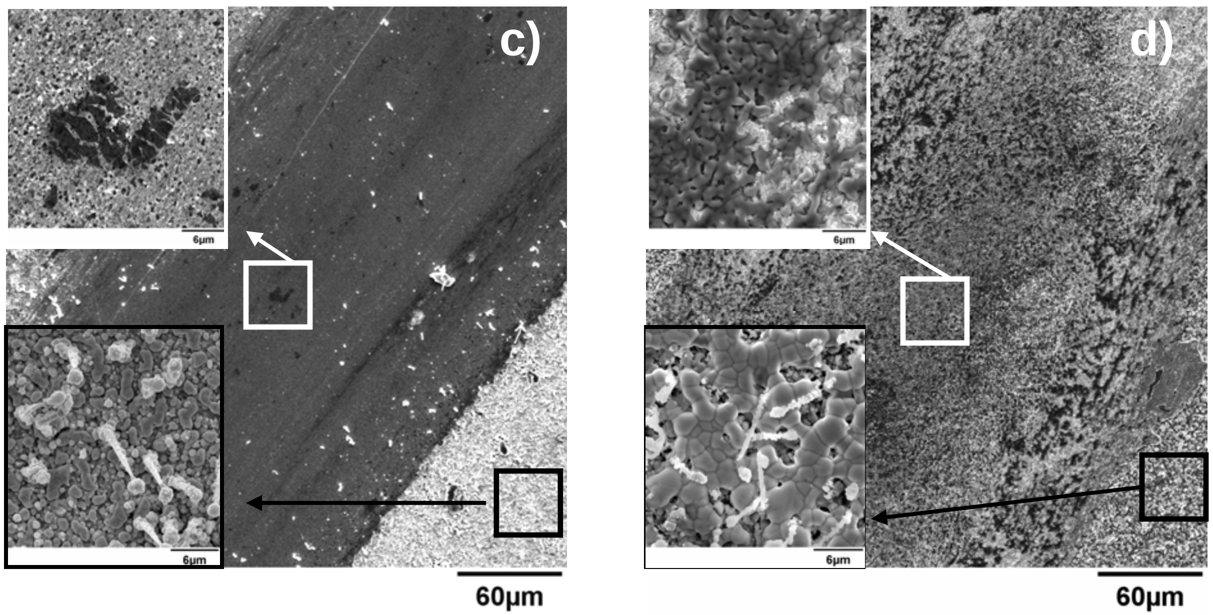
Figures 1 c and d



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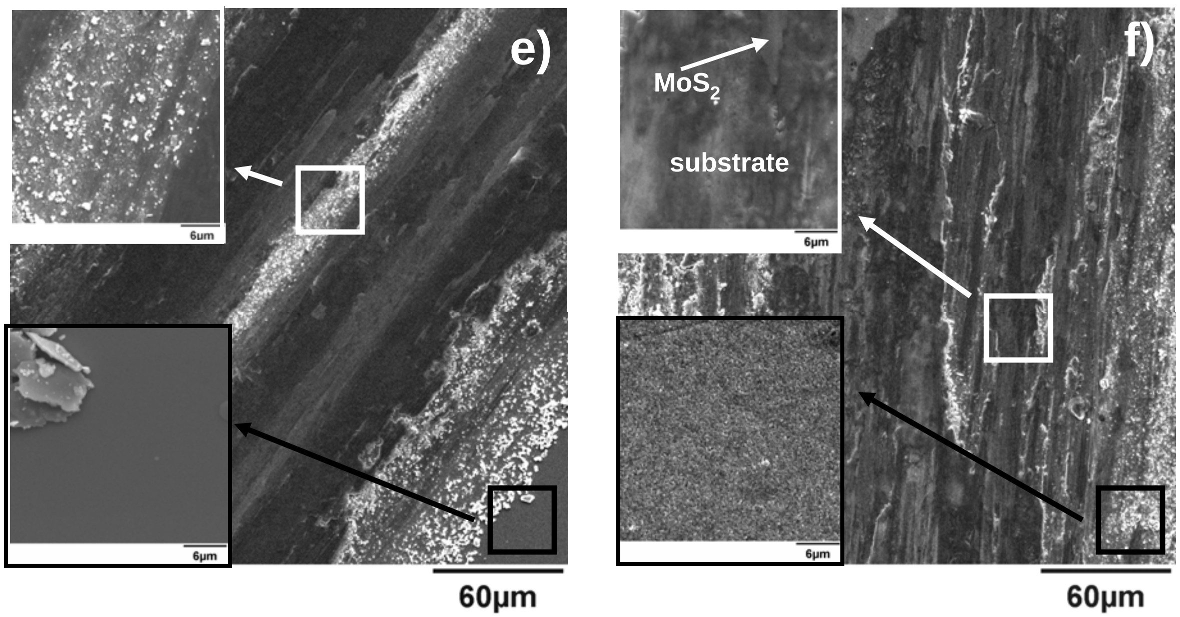
Figures 1 e and f



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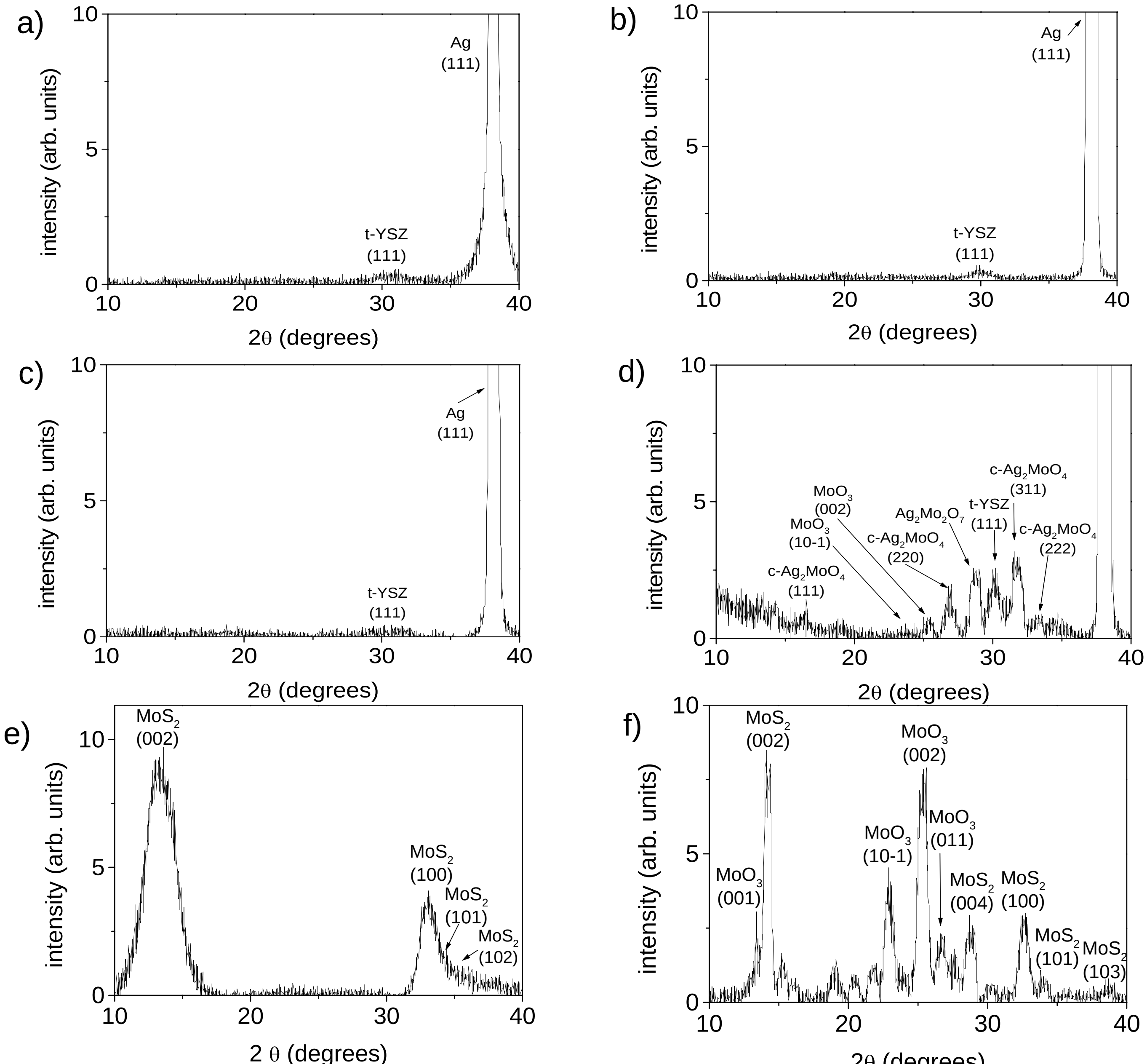
Figures 2 a-f



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Figures 3 a,b and c